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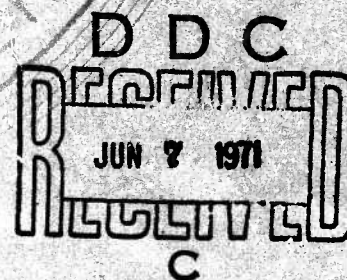
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LONG-RANGE ORDER IN β -BRASS

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MATERIALS SCIENCES DIVISION

May 1971



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Technical Report by

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Long-Range Order in β -Brass*

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The long-range order in β -brass has been determined from x-ray measurements of integrated intensities of superlattice reflections. Analysis of the data includes allowance for the observed appreciable difference between the two Debye-Waller factors. The long-range order parameter is found to be significantly greater than the values from current Ising-model calculations over a wide range of temperatures below the critical region.

The order-disorder transformation in β -brass is well known as one of the few such transformations that apparently are continuous, lambda-like phase transformations.¹ Recent experiments²⁻⁶ have shown that at temperatures near the critical temperature, $T_c \sim 468^\circ\text{C}$, a number of its characteristics are described quite well by the bcc Ising model. We present here the results of an x-ray diffraction study which show that over a wide range of temperatures outside the critical region the long-range order in this alloy is consistently significantly greater than that predicted by current Ising-model calculations.⁷⁻⁹ Results differing from ours obtained in a recent neutron-diffraction experiment by Norvell and Als-Nielsen¹⁰ appear to contain appreciable systematic errors, as discussed below.

The object of our investigation was to determine the long-range order parameter S for β -brass over the entire range of temperatures below T_c , to improve on the twenty-year-old results of Chipman and Warren.¹¹ This parameter is obtained from superlattice Bragg reflections, whose intensity varies approximately as

$$I \propto S^2 |f_{Zn} \exp(-M_{Zn}) - f_{Cu} \exp(-M_{Cu})|^2, \quad (1)$$

where f_x is the scattering factor of an atom of type x at rest, and M_x is its Debye-Waller exponent, proportional to its mean square amplitude of thermal vibration, which we treat initially as depending only on the identity of the atom. Thus our primary experiment was to measure the integrated intensities of both the (100) and the (300) superlattice reflections at temperatures ranging from liquid helium up to T_c .

The x-ray diffraction apparatus used Cu $K\alpha$ radiation obtained with a doubly bent LiF monochromator from an x-ray tube operated at 20 mA and 14 kV peak (eliminating $\frac{1}{2}\lambda$ and other harmonics). The specimen was a single crystal containing 51.9 at.% Cu, with a mosaic spread of only a few minutes, with flat faces parallel to

(100) planes. Scintillation-detector counting systems measured the diffracted radiation and monitored the primary beam, the latter allowing all measurements to be adjusted to constant incident-beam power. Temperatures were measured by thermocouples, calibrated at liquid He and N_2 or T_c , mounted against the edge of the front face of the specimen. A proportional controller maintained the furnace temperature within 0.1°C over the time for a single measurement. A helium atmosphere was used in the furnace.

Integrated intensities were measured using the ω -scan technique. Our standard procedure was to measure the integrated intensity of each reflection at room temperature both before and after a short series of measurements at high (low) temperatures, and then to normalize the integrated intensity of a reflection at temperature T in terms of its room-temperature value. At the higher temperatures the experimental runs were made shorter and shorter to minimize possible effects due to zinc loss by evaporation.

The effects of zinc loss on our integrated intensities were investigated in two ways: by comparing the "before" and "after" room-temperature measurements bracketing each high-temperature run, and by comparing integrated intensities obtained at the same temperatures after different thermal histories. The comparisons of "before" and "after" values, each reproducible to 0.2%, for the runs above 300°C showed the "after" values generally to be slightly smaller, with a rms difference of 0.6% and a maximum difference of 1.4%. The comparisons of at-temperature data for different thermal histories, though less accurate, showed similar results: In the worst case, for a run containing two standard 30-min periods of measurement at 425°C separated by 10 min going up to T_c and back, the second set of (100) and (300) intensities at 425°C were smaller than the first by 0.4 and 2.0%, respectively, with an experimental precision for each of 1.0%.

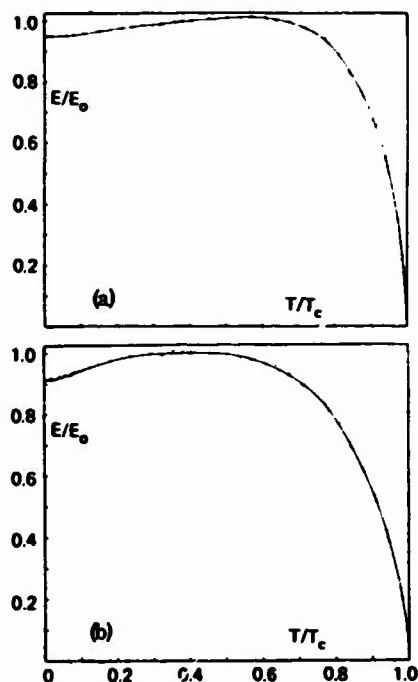


FIG. 1. (a) The measured integrated intensity E of the (100) reflection, normalized by its room-temperature value E_0 , as a function of T/T_c . (b) As in (a), but for the (300) reflection.

We conclude from these checks that errors in our intensity data due to zinc-loss effects are less than 1% even at the highest temperatures.

The measured values of the normalized integrated intensities, E/E_0 , of the (100) and (300) reflections are plotted in Figs. 1(a) and 1(b), respectively, as a function of the reduced temperature T/T_c . Room temperature, where $E/E_0 = 1$, is at $T/T_c = 0.40$. Most of the data points below $T/T_c = 0.85$ correspond to an average of six measurements and show a reproducibility varying from approximately $\frac{1}{4}\%$ below room temperature to $\frac{1}{2}\%$ at $T/T_c = 0.85$. The remaining points are for fewer and/or shorter measurements, with correspondingly larger errors. The curves are smooth averages used in the subsequent analysis.

The high-temperature behavior of these intensities is that expected as the long-range order goes continuously to zero at T_c . At low temperatures, however, where the long-range order is constant, the intensities of both reflections are observed to decrease with decreasing temperature, which shows unambiguously from Eq. (1) that, since $f_{Zn} > f_{Cu}$, at these temperatures the mean square amplitude of thermal vibration of a Cu atom in this alloy must be appreciably greater than that of a Zn atom. The magnitude of this effect is more obvious when we point out that the

change in the average mean square amplitude of vibration¹² on lowering the temperature from $T/T_c = 0.40$ to $T/T_c = 0.0$ would cause the intensities of the (100) and (300) reflections to increase by 4.3 and 45.6%, respectively, if the amplitudes of vibration of the two atoms were equal. We have estimated from these data that at room temperature the mean square amplitude of vibration of a Cu atom is approximately 12% larger than that of a Zn atom, and this difference has been confirmed by Nicklow and Dolling¹³ from computer calculations using the force-constant values for β -brass measured by Gilat and Dolling.¹⁴ This effect has not been recognized in any previous study of this alloy.

Values of these normalized integrated intensities taken at regular temperature intervals from the smooth average curves were corrected for the usual factors of extinction, included diffuse scattering, and a Debye-Waller factor representing the average mean square amplitude of vibration. The largest correction, that for the mean Debye-Waller factor, was determined in an auxiliary experiment¹⁵ from measurements of the (310) fundamental reflection from a polycrystalline specimen over this same range of temperatures. The included thermal diffuse scattering was calculated using an improved approach¹⁵ that correctly treats anisotropic factors. The included critical scattering, negligible except for $T/T_c > 0.90$, was calculated on the basis of the Ising model. The extinction correction, at its worst only 3.5% for the (100) and 2.0% for the (300), was calculated using the theory of Zachariasen¹⁶ together with absolute intensity measurements of the (200) and (310) fundamental reflections from our crystal.

Now let the square root of the corrected, normalized, integrated intensities of any two superlattice reflections at a given temperature be denoted by A_1 and A_2 , respectively. From Eq. (1) one can write

$$A_i \approx \frac{S}{S_0} \left| \frac{(f_{Zn} - f_{Cu}) + (f_{Zn} + f_{Cu})(M\delta)}{(f_{Zn} - f_{Cu}) + (f_{Zn} + f_{Cu})(M\delta)_0} \right|, \quad (2)$$

where

$$2M\delta = M_{Cu} - M_{Zn} \text{ and } 2M = M_{Cu} + M_{Zn},$$

and where S_0 and $(M\delta)_0$ are values at room temperature. The neglect here of the higher terms in the expansions of $\exp(\pm M\delta)$ is a good approximation for our experiment, the maximum error in A_i being only 0.06%. Then by manipulat-

ing Eq. (2) one can show that at any temperature

$$S/S_0 = (A_1 - RA_2)/(1-R), \quad (3)$$

where R is a constant involving scattering factors and $(M5)_0$. For temperatures below room temperature, where $S \approx S_0$, this gives

$$R \approx (A_1 - 1)/(A_2 - 1). \quad (4)$$

Thus by using Eq. (3), with a value of R derived from the low-temperature data with Eq. (4), we can determine S/S_0 as a function of temperature from our data without having to know the values of the scattering factors or the difference between the two Debye-Waller exponents. We note also that two alternative forms for Eq. (1), reflecting different assumptions concerning the thermal vibrations – such as, for example, associating different mean square amplitudes of vibration with the two sublattices rather than the two kinds of atoms – are found to lead to the same Eqs. (3) and (4), so the analysis is not sensitive to that initial assumption.

The result for the normalized long-range-order parameter, S/S_0 , as a function of temperature obtained from our (100) and (300) data is plotted as the solid curve in Fig. 2. The value is constant within 0.1% for $T/T_c < 0.46$. The calculated random error in this parameter increases with temperature from approximately 1/2% at $T/T_c = 0.6$ to 1% at $T/T_c = 0.9$. The data for both reflections were required to obtain this one curve, with no redundancy, so as a check we have made a short set of integrated intensity measurements on a third superlattice reflection,

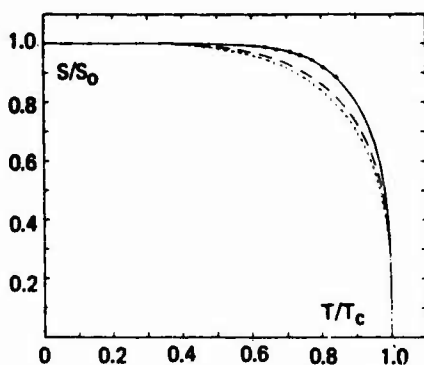


FIG. 2. The normalized long-range-order parameter, S/S_0 , as a function of T/T_c . Experimental results are given by the solid curve, from the (100) and (300) data, and by the points, from (100) and (210) data. The short-dashed curve gives the "rigid" Ising calculation of Essam and Fisher (Ref. 7), and the long-dashed curve gives the "compressible" Ising calculation of Baker and Essam (Refs. 8 and 9).

the (210). Proceeding as before, and joining these data with the corresponding (100) data in the analysis, we have obtained the values for S/S_0 plotted as the points in Fig. 2. The agreement between these points and the solid-curve result is excellent, the greatest discrepancy being only 0.2%.

The two other curves in Fig. 2 show recent bcc Ising-model calculations. The short-dashed curve presents the [10, 10] Padé approximant of Essam and Fisher,⁷ and the long-dashed curve gives the results of the recent "compressible" Ising-model calculation of Baker and Essam.^{8,9} Our measurements differ markedly from both calculations, the difference being an order of magnitude larger than the experimental error at $T/T_c = 0.9$, for example, and the disagreement extends consistently over a wide range of temperatures.

Norvell and Als-Nielsen¹⁰ recently measured the long-range order in β -brass using neutron-diffraction techniques and obtained results in good agreement with the Baker-Essam calculation, contrary to our findings. However, in that experiment the difference between the Debye-Waller exponents was not recognized, the corrections for extinction were quite large and thus not dependable, and the correction for the mean Debye-Waller factor was determined by a self-consistent procedure and does not agree with our measured values, so we suggest that such factors have led to serious systematic errors in their results.

In the critical region very near T_c , where other experiments²⁻⁶ on β -brass have generally shown good agreement with the Ising model, our measurements are not yet sufficient to allow a quantitative comparison with theory. Outside this region ($T/T_c < 0.97$) our results show that the long-range order in β -brass differs considerably from Ising-model calculations. The obvious suggestion is that this difference is due partly to the departure from stoichiometry and partly to the possible long-range forces that characterize the real alloy.

*A preliminary report on this work was presented at the Battelle Colloquium on Critical Phenomena, Gstaad, Switzerland, September 1970.

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